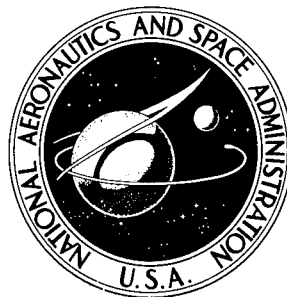


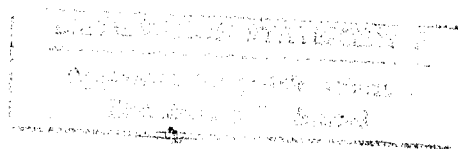
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THERMALLY STABLE POLYIMIDES  
FROM SOLUTIONS OF MONOMERIC REACTANTS

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# THERMALLY STABLE POLYIMIDES FROM SOLUTIONS OF MONOMERIC REACTANTS

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Lewis Research Center

## SUMMARY

A new approach for the synthesis of processable polyimides was developed. In this approach graphite-fiber-reinforced composites were fabricated from fibers impregnated with solutions of appropriate monomers rather than from amide-acid prepolymer solutions. The monomers used were (1) a dimethyl ester of an aryl tetracarboxylic acid, (2) an aryl diamine, and (3) the monomethyl ester of nadic acid. Composites fabricated by using the monomeric solutions were tested at 315° C (600° F) for weight retention, flexural strength, flexural modulus, and interlaminar shear.

The monomers were soluble in low-boiling alcoholic solvents such as methanol. The solutions of monomers offer the following advantages over amide-acid prepolymer solutions: (1) excellent shelf life, (2) increased solubility, and (3) low solution viscosity.

The mechanical properties and thermal stability characteristics of graphite-fiber-reinforced composites made from solutions of monomers compared favorably to those of composites made from amide-acid prepolymer solutions.

## INTRODUCTION

During the last decade polymer chemists have succeeded in synthesizing numerous polymers which, for organic materials, exhibit outstanding thermal stability. The key to synthesizing these so-called high-temperature polymers has been to use highly stable structural units such as aromatic and/or heterocyclic rings. Unfortunately, the structural units which confer thermal stability to high-temperature polymers are also responsible for their inherent insolubility and infusibility, commonly referred to as intractability. The intractable nature of these polymers makes it very difficult - nearly impossible - to use them as matrix resins in advanced composites.

An approach of chemically modifying the structure of polyimide prepolymers as a means of improving the processability was reported by Delvigs, Hsu, and Serafini (ref. 1) and Serafini (ref. 2). Although the chemically modified prepolymers were found to be more resistant to premature imidization, the long chain nature of the prepolymers prevented adequate resin flow during final processing. Lubowitz (ref. 3) and Burns, Jones, Vaughan, and Kendrick (ref. 4) used the approach of preparing low-molecular-weight end-capped amide-acid (polyimide) prepolymers that polymerized into thermally stable polyimides without the evolution of byproducts. A commercially available resin of this type is known as P13N. Another version, known as P10P, having considerably improved thermooxidative stability has been developed (ref. 5). From our in-house studies with P10P as a matrix resin we have observed that the P10P prepolymer solutions exhibit a very limited shelf life at room temperature, as evidenced by precipitation and/or gel formation. Prior to the appearance of the precipitate or gel there is a steady decrease of solution viscosity. The significance of this has been discussed by Delvigs, Hsu, and Serafini (ref. 1).

This report describes a new approach for the synthesis of processable polyimides. Graphite-fiber-reinforced composites are fabricated from fibers impregnated with solutions of appropriate monomers rather than from amide-acid prepolymer solutions. The mechanical properties and thermal stability characteristics of composites made from a selected solution of monomers are compared to the identical properties for composites made from P10P prepolymer solutions.

## EXPERIMENTAL PROCEDURE

### Monomers

The monomers used in this study are shown in figure 1. The monomers 4, 4'-methylenedianiline (I) and 4, 4'-thiodianiline (II) were obtained from a commercial source and recrystallized from 2-propanol.

The monomethyl ester of 5-norbornene-2, 3-dicarboxylic acid (III) was prepared according to the method of Walton (ref. 6).

The 2, 5-dicarbomethoxyterephthalic acid (IV) was prepared according to Bell and Jewell (ref. 7).

Dimethyl ester of 3, 3', 4, 4'-benzophenonetetracarboxylic acid (V) was synthesized by refluxing a suspension of 3, 3', 4, 4'-benzophenonetetracarboxylic dianhydride (64.4 g,  $2.00 \times 10^{-1}$  mole) in dry methanol (60 cm<sup>3</sup>) until the solid had dissolved (2 hr) and then for an additional hour. Excess methanol was evaporated under reduced pressure at 50° C. The yellowish oil was dried in vacuum ( $10^{-3}$  torr) at room temperature for 24 hours to give 76.8 g (99 percent) of the isomer mixture (V) as a crystalline solid.

## Prepreg Solutions

The P10P amide-acid prepolymer solution was prepared according to the method of Burns, Jones, Vaughan, and Kendrick (ref. 5) at a solids content of 40 percent by weight.

Solutions of monomers were prepared by dissolving a mixture of the reactants in the mole ratios indicated in table I in either anhydrous N, N-dimethylformamide (DMF) or anhydrous methanol at room temperature. The solutions were prepared at a solids content of 60 percent by weight.

## Viscosity Determination

Freshly prepared solutions in DMF with a solids content of 20 percent by weight were introduced into calibrated Ubbelohde viscometers. Periodic viscosity measurements were taken. The solutions were stored at 25° C in the capped viscometers for the duration of the experiment.

## Composite Fabrication and Testing

Prepreg tapes were made by drum-winding and impregnating Hercules HTS graphite fiber with the various solutions of monomeric reactants and with P10P prepolymer solution in such proportions that the prepreg contained 40 percent resin and 60 percent fiber by weight. The prepregs made from the monomers or prepolymers dissolved in DMF were heated for 1 hour at 55° C (130° F) and then 10 minutes at 121° C (250° F) to reduce the solvent content to 5 to 10 percent by weight. The prepregs made from the monomers dissolved in methanol were heated for 2 hours at 55° C (130° F). The prepreg tapes at this point were flexible, but not tacky.

Unidirectional composites were molded by using the method of Burns, Jones, Vaughan, and Kendrick (ref. 5). Six-ply laminates 1.27 by 12.4 centimeters (1/2 by 4 7/8 in.) or 7.62 by 25.4 centimeters (3 by 10 in.) were molded. No attempt was made to optimize the fabrication procedure.

Test specimens were cut from the composites and the properties evaluated. Two measurements were taken at each condition and averaged to obtain the data shown in figures 4 to 7. Three or more tests at each condition were averaged to obtain the data shown in figures 8 to 11. Determinations of flexural strength and modulus were performed in accordance with ASTM method D790. Shear strength was determined by using the short-beam flexural test procedure with a span-to-depth ratio of 5. All 315° C (600° F) tests were performed after a 15-minute soak at 315° C (600° F). The 315° C

(600° F) isothermal aging of the composites was conducted in a forced-air oven with an air change rate of 100 cubic centimeters per minute.

## RESULTS AND DISCUSSION

Conventional condensation type aryl polyimides are synthesized by the reaction of an aryl dianhydride with an aryl diamine in a polar solvent. In the first step of the reaction a high-molecular-weight polyamide-acid prepolymer is formed. In the second step, water is eliminated by thermal and/or chemical means to form the cyclic polyimide. Composite processing difficulties encountered with condensation type polyimides are caused primarily by the volatilization of the reaction by-products formed during the second step of the reaction.

One of the major breakthroughs in the chemistry of high-temperature resins was the development of a novel class of polyimides which cure by an addition reaction (refs. 3 and 4). This approach utilizes low-molecular-weight amide-acid prepolymers end-capped with reactive alicyclic rings. The molecular structures of the amide-acid and imidized prepolymers of the version known as P10P are shown in figure 2. Details concerning the synthesis, "B-staging," and final cure are given in reference 5. The version known as P13N has gained wide acceptance as a processable, thermally stable polyimide. Prepolymer P10P differs from P13N in the following two respects: (1) P10P has a formulated molecular weight of 1000 compared to 1300 for P13N, and (2) the dianhydride used in P10P is pyromellitic dianhydride (PMDA) rather than 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA). As expected, the thermooxidative stability of P10P is superior to that of P13N (ref. 5).

A major shortcoming of P10P amide-acid prepolymer solutions is that they exhibit a very limited and variable shelf life. We have observed gelation and/or precipitation to occur in solutions containing 40 percent solids within 2 days at room temperature. None of the monomeric solutions employed in this study have exhibited similar behavior. A monomeric solution containing 60 percent solids and stored at ambient conditions for 6 months appears to be unchanged.

The variation of solution viscosity for both an amide-acid prepolymer solution and a monomeric solution is shown in figure 3. The monomeric solution was formulated to approximate the composition of P10P. The gradual increase of viscosity for the monomeric solution (lower curve of fig. 3) indicates that the monomers do undergo some prereaction in solution. The viscosity increase can be attributed to the formation of low-molecular-weight oligomers which do not appreciably alter the solution viscosity and shelf life. In contrast, the solution viscosity of the P10P prepolymer solution (upper curve of fig. 3) markedly decreased. We hypothesize that hydrolytic degradation of the amide-acid prepolymer chains occurs continuously and results in the sharp decrease in

solution viscosity. It is interesting to note that, in order to make the viscosity measurements over a reasonable period of time, it was necessary to use relatively dilute (20 percent solids) solutions. Solutions having solids content in the range of 30 to 40 percent gelled and/or precipitated in a few days.

To evaluate the general applicability of the approach of using solutions of monomeric reactants to impregnate fiber reinforcements, six monomer solutions differing in chemical compositions and/or stoichiometry were prepared in DMF by using the monomers shown in figure 1. The chemical composition, molar ratio of the reactants, and some properties of 1.27- by 12.4-centimeter ( $1/2$ - by  $4\frac{7}{8}$ -in.) graphite-fiber composites are summarized in table I. Sample A was formulated to have the chemical composition and stoichiometry of P10P. Samples C and D are chemically similar to P13N; however, their stoichiometry was adjusted to approximate prepolymers having formulated molecular weights of 1500 and 3000, respectively.

It should be pointed out that all of the data (weight loss, flexural strength and modulus, and interlaminar shear strength) presented in this report were obtained from laminates fabricated according to a procedure which had been optimized for amide-acid prepolymer solutions rather than monomeric reactant solutions.

The room temperature and  $315^{\circ}\text{C}$  ( $600^{\circ}\text{F}$ ) interlaminar shear strengths of composites made from the monomeric solution (sample A) corresponding to P10P compare favorably to the values obtained from P10P prepolymers.

The variation in interlaminar shear strengths and weight loss resulted primarily from differences in the resin flow characteristics of the various monomer systems. In general, poor resin flow resulted from decreasing the molar ratio of the alicyclic end caps (III) in the monomeric solution.

The 600-hour,  $315^{\circ}\text{C}$  ( $600^{\circ}\text{F}$ ) composite weight loss data for samples A and B (18 percent) compare favorably with the 500-hour,  $315^{\circ}\text{C}$  ( $600^{\circ}\text{F}$ ) weight loss (14 percent) for the P10P - T50S-graphite-fiber composite (ref. 5) and with the data presented for P10P composites in figure 4. The composite weight loss of sample C was lower than anticipated. This could be due to enhanced resin flow resulting in a very low void content coupled with a lower alicyclic content. The superior thermal stability of the polyimide composite made with BTDA as the dianhydride moiety, compared to that made with the PMDA moiety (weight loss sample C < weight loss sample A) appears to be contradictory to the findings reported in reference 5. Apparently in the studies reported in reference 5, the greater thermal stability of the PMDA compared to BTDA overshadowed the higher alicyclic content of P10P (30 percent higher than for P13N). However, for sample C the further reduction of alicyclic content (13 percent lower alicyclic content than for P13N) enhanced the thermal stability to a greater degree than the inclusion of PMDA in P10P. Currently resins having the chemical composition of sample C are being evaluated to determine the optimum molar ratios of the reactants.

The physical and mechanical properties of composites made from P10P amide-acid solution and monomeric solution A were compared over an extended period of time at 315° C (600° F). The results of the isothermal aging are shown in figure 4. The composite weight losses are essentially identical, which indicates that the thermooxidative stability is not lowered by the use of monomeric solutions.

The effect of thermal aging on flexural strength is illustrated in figure 5. The flexural strength of the P10P composite was somewhat higher, at least partly because of a higher fiber content (54 as opposed to 52 vol. % for sample A). However, the change in flexural strength in going from room temperature to 315° C (600° F) and during the isothermal aging was similar for both composite systems. The effect of temperature and isothermal aging on the flexural modulus of elasticity is shown in figure 6. After an exposure at 315° C (600° F) for 15 minutes the 315° C (600° F) modulus was lower than the room-temperature modulus for unaged samples. It is interesting to note that the modulus decreased during the initial 150 hours, whereas the flexural strength increased during this time interval.

The variation of interlaminar shear strength with time at 315° C (600° F) is shown in figure 7. There was a decrease of approximately 40 percent in the interlaminar shear strength in going from room temperature to 315° C (600° F). However, after the initial decrease, the interlaminar shear remained almost constant for more than 300 hours. The values were similar for the two composite systems, with the small differences attributed to variations in the resin content of the composites.

To determine if monomeric solutions could be used to fabricate larger panels, 7.62- by 25.4-centimeter (3- by 10-in.) panels were molded by using monomeric solution A in DMF. Unexpectedly, all panels had numerous small blisters on the surface and a relatively high void content. This seemed to indicate incomplete removal of volatiles during the drying and imidization steps. An increase in the imidization time from 2 to 5 hours at 216° C (400° F) lessened, but did not entirely eliminate, the blistering. However, substitution of methanol for the higher boiling DMF consistently resulted in void-free composites.

In figures 8 to 11 properties of these 7.62- by 25.4-centimeter (3- by 10-in.) graphite-fiber composites made from monomeric solution A are compared to similar properties for composites from P10P amide-acid prepolymer solutions. The data for the P10P composites are taken from Hanson and Serafini (ref. 8). The composite weight loss at 315° C (600° F) (fig. 8) exhibited a similar decrease for both resin systems and is almost identical to the results obtained for the 1.27- by 12.4-centimeter (1/2- by 4 7/8-in.) composites shown in figure 4.

The flexural strength of both composite systems decreased on exposure to air at 315° C (600° F) (fig. 9). The initial increase in flexural strength at 315° C (600° F) shown in figure 5 was not observed. This increase might have resulted from a more complete removal of solvent residuals from the smaller panels prior to molding.



The flexural modulus of elasticity (fig. 10) decreased continuously on exposure at 315° C (600° F). The flexural modulus of the composite made from monomeric solution A was approximately 17 percent lower than the flexural modulus of the composite made from the P10P amide-acid prepolymer solution. It can be seen in figure 10 that the rate of decrease of the modulus was nearly identical for both composites. This indicates that the fabrication procedures might have caused the initial differences in the moduli.

The interlaminar shear strength of the two composite systems as a function of exposure time at 315° C (600° F) is shown in figure 11. The figure shows that both composites exhibited a similar decrease (approximately 36 percent) in interlaminar shear strength after 600 hours at 315° C (600° F).

From the results presented in figures 8 to 11 it can be seen that high-quality, void-free composites can be fabricated from monomeric solutions. It is expected that this approach could be used to fabricate actual hardware components.

## CONCLUSIONS

The following conclusions were drawn from the results of an investigation of the method of preparing thermally stable polyimides from solutions of monomeric reactants:

1. Solutions of monomeric reactants for the synthesis of processable polyimides can be used for various combinations of appropriate monomers and solvents.
2. Solutions of monomeric reactants offer the following advantages over amide-acid prepolymer solutions:
  - (a) Excellent shelf life
  - (b) Compatibility with low-boiling nontoxic alcoholic solvents (e. g. , methanol)
  - (c) Increased solubility (solutions containing 60 to 70 percent solids by weight are readily obtainable)
  - (d) Low solution viscosity
3. The mechanical properties and thermal stability characteristics of graphite-fiber-reinforced composites made from solutions of monomeric reactants compare favorably to those of composites made from amide-acid prepolymer solutions.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, October 5, 1971,  
134-03.

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TABLE I. - PROPERTIES OF VARIOUS 1.27- BY 12.4-CENTIMETER (1/2- BY 4<sup>7</sup>/<sub>8</sub>-IN.) POLYIMIDE -  
GRAPHITE-FIBER COMPOSITES MADE FROM MONOMERIC SOLUTIONS

Sample	Monomeric solution composition <sup>a</sup>	Mole ratio of reactants	Interlaminar shear <sup>b</sup> at 24° C (75° F)		Interlaminar shear <sup>b</sup> at 315° C (600° F)		Composite weight loss <sup>c</sup> after 600 hours in air at 315° C (600° F), percent
			N/m <sup>2</sup>	psi	N/m <sup>2</sup>	psi	
A	III/I/IV	2/2.34/1.34	74.47	10 800	42.75	6200	17.6
B	III/I/IV	2/4.32/3.32	-----	-----	34.30	4975	17.8
C	III/I/V	2/3.09/2.09	105.49	15 300	41.37	6000	9.5
D	III/I/V	2/6.19/5.19	-----	-----	35.44	5140	28.0
E	III/II/IV	2/3.49/2.49	57.92	8 400	-----	-----	22.6
F	III/II/V	2/3.97/2.97	-----	-----	15.96	2315	20.6

<sup>a</sup>I, 4,4'-methylenedianiline; II, 4,4'-thiodianiline; III, monomethyl ester of 5-norbornene-2,3-dicarboxylic acid; IV, 2,5-dicarbomethoxyterephthalic acid; V, dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid.

<sup>b</sup>Average of two to four tests.

<sup>c</sup>Average from two composites.

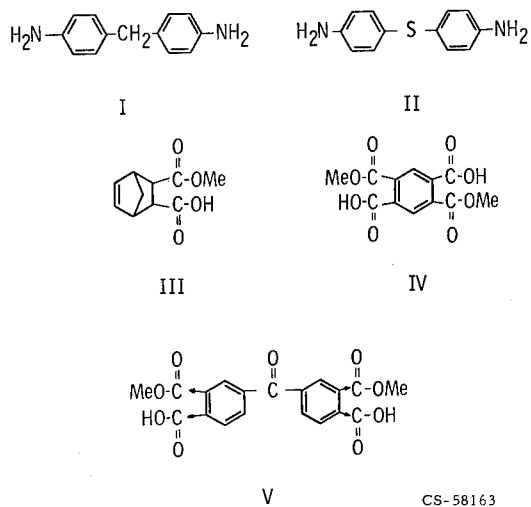


Figure 1. - Monomers used for preparation of monomeric solutions.

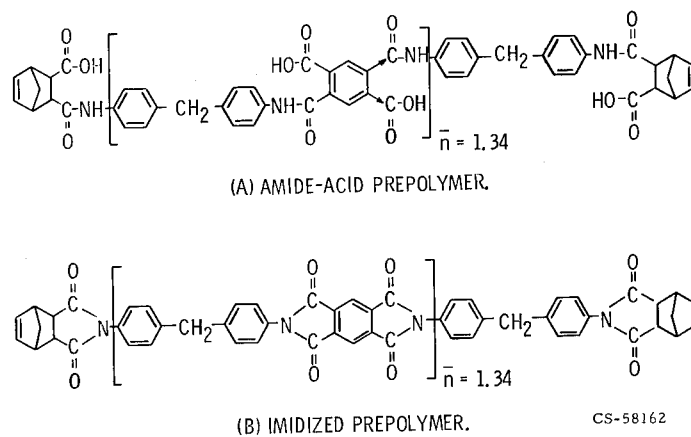


Figure 2. - P10P prepolymers.

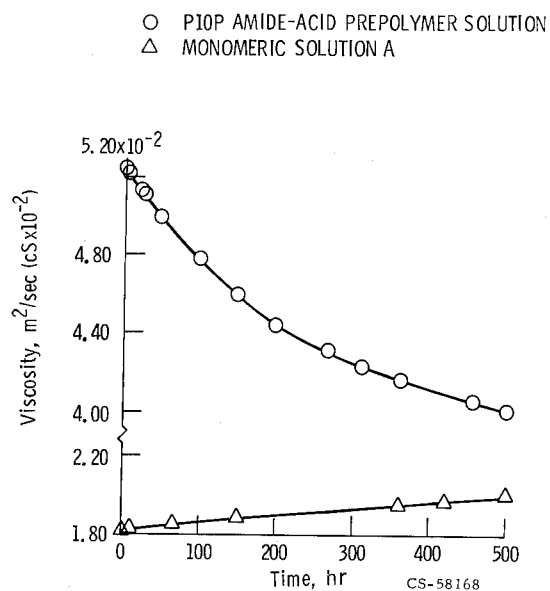


Figure 3. - Viscosity changes of P10P amide-acid and monomeric solution A. Solutions prepared in DMF at room temperature; solids content, 20 weight percent.

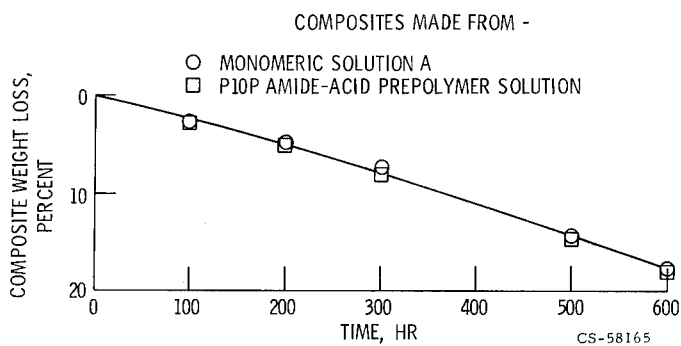


Figure 4. - Percent weight loss of 1.27- by 12.4-centimeter (1/2- by 4 7/8-in.) polyimide - HTS-graphite-fiber composites aged in air at 315° C (600° F).

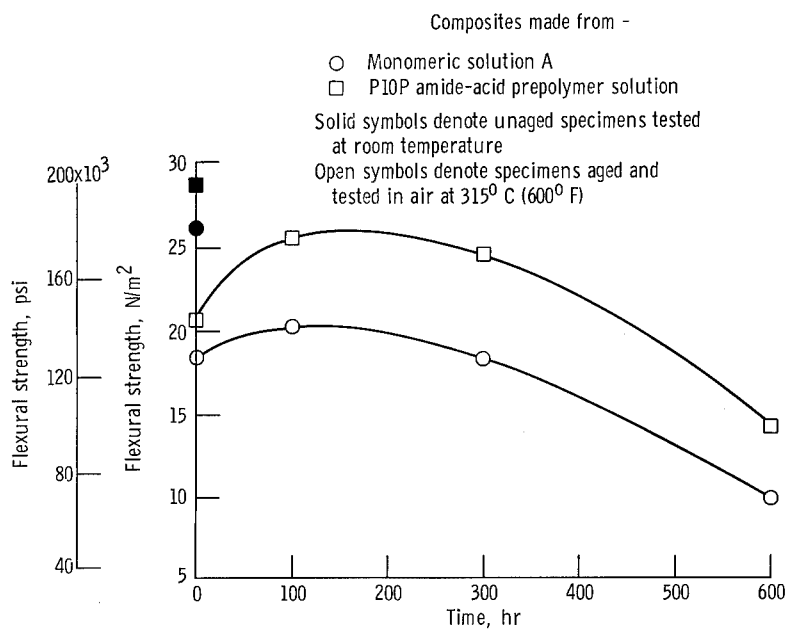


Figure 5. - Flexural strength of 1.27- by 12.4-centimeter (1/2- by 4 7/8-in.) graphite-fiber composites.

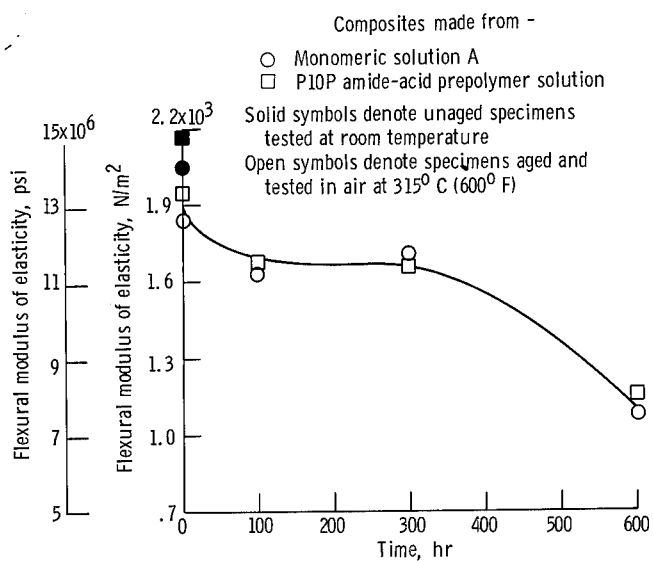


Figure 6. - Flexural modulus of elasticity of 1.27- by 12.4-centimeter (1/2- by 4 7/8-in.) polyimide-HTS-graphite-fiber composites.

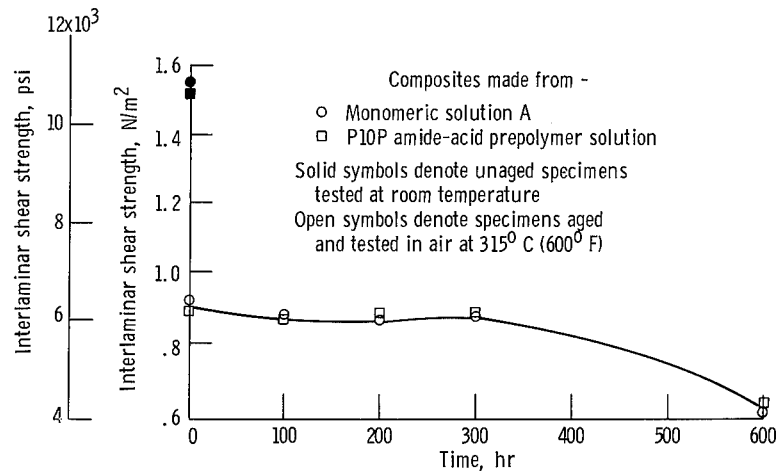


Figure 7. - Interlaminar shear strength of 1.27- by 12.4-centimeter (1/2- by 4<sup>7</sup>/<sub>8</sub>-in.) polyimide - HTS-graphite-fiber composites.

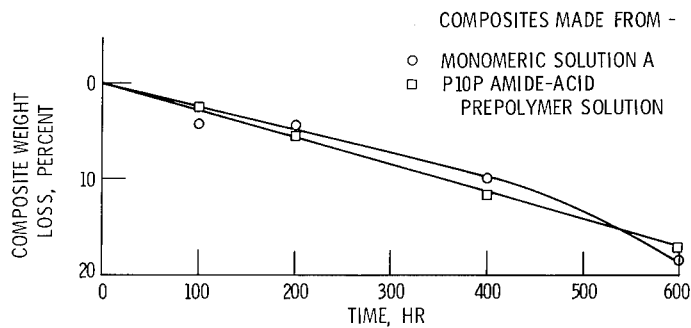


Figure 8. - Percent weight loss of 7.62- by 25.4-centimeter (3- by 10-in.) polyimide - HTS-graphite-fiber composites aged in air at 315° C (600° F).

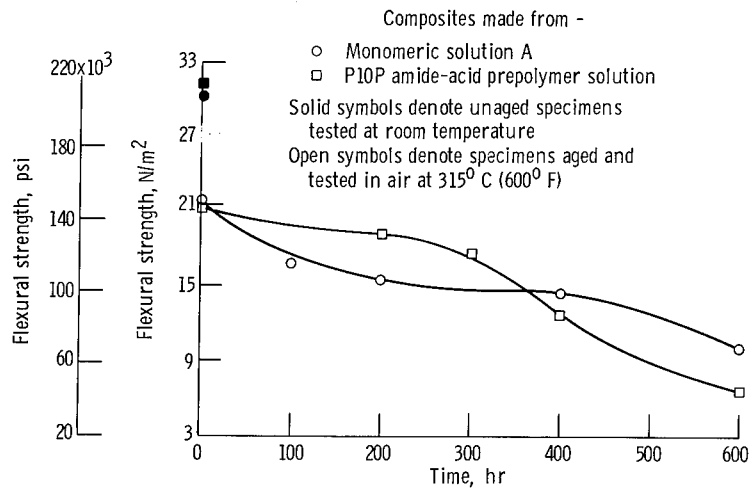


Figure 9. - Flexural strength of 7.62- by 25.4-centimeter (3- by 10-in.) polyimide - HTS-graphite-fiber composites.

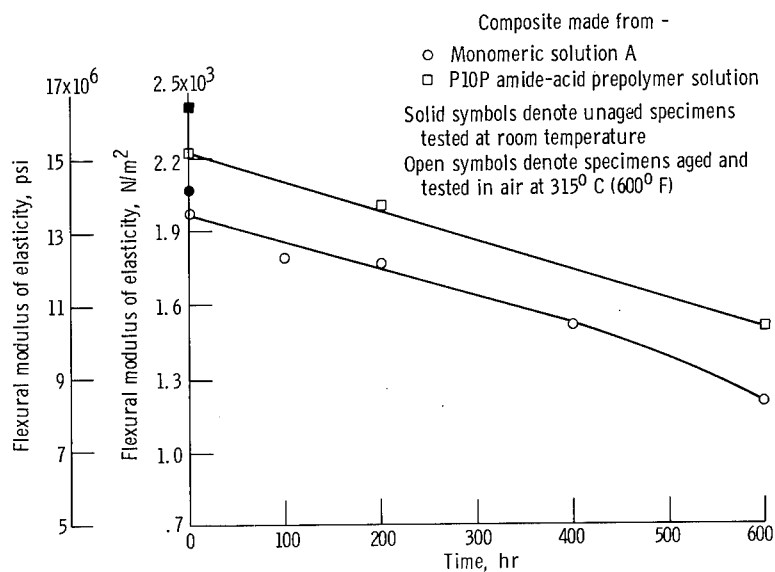


Figure 10. - Flexural modulus of elasticity of 7.62- by 25.4-centimeter (3- by 10-in.) polyimide - HTS-graphite-fiber composites.

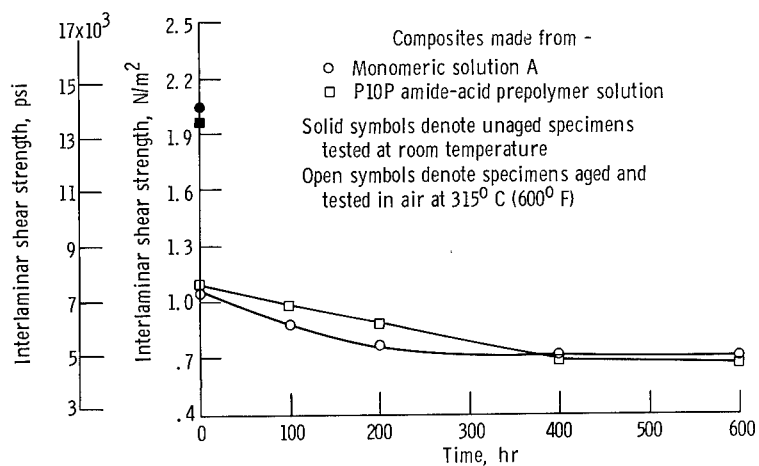


Figure 11. - Interlaminar shear strength of 7.62- by 25.4-centimeter (3- by 10-in.) polyimide - HTS-graphite-fiber composites.

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